HYDROGEN IN MARTIAN METEORITES. A. H. Peslier[1], R. Hervig[2], and T. Irving[3], [1]Jacobs, NASA-Johnson Space Center, Mail Code X13, Houston TX 77058, USA, anne.h.peslier@nasa.gov, [2]School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, USA, [3]Dept. of Earth & Space Sciences, University of Washington, Seattle, WA, USA.

Introduction:

Most volatile studies of Mars have targeted its surface via spacecraft and rover data, and have evidenced surficial water in polar caps and the atmosphere, in the presence of river channels, and in the detection of water-bearing minerals [e.g., 1-5]. The other focus of Martian volatile studies has been on Martian meteorites which are all from its crust. Most of these studies are on hydrous phases like apatite, a late-stage phase, i.e. crystallizing near the end of the differentiation sequence of Martian basalts and cumulates [e.g., 6-9]. Moreover, calculating the water content of the magma a phosphate crystallized from is not always possible [10], and yet is an essential step to estimate how much water was present in a parent magma and its source.

Water, however, is primarily dissolved in the interiors of differentiated planets as hydrogen in lattice defects of nominally anhydrous minerals (olivine, pyroxene, feldspar) of the crust and mantle [11,12]. This hydrogen has tremendous influence, even in trace quantities, on a planet's formation, geodynamics, cooling history and the origin of its volcanism and atmosphere as well as its potential for life. Studies of hydrogen in nominally anhydrous phases of Martian meteorites are rare [13,14]. Measuring water contents and hydrogen isotopes in well-characterized nominally anhydrous minerals of Martian meteorites is the goal of our study. Our work aims at deciphering what influences the distribution and origin of hydrogen in Martian minerals, such as source, differentiation, degassing and shock.

Methods:

Measuring water in Martian meteorite minerals is challenging because the minerals are fragile and riddled with fractures from impact processes that makes them break apart during sample processing. Moreover, curing the sample in epoxy causes problems for the two main water analysis techniques, Fourier transform infrared spectrometry (FTIR) and secondary ionization mass spectrometry (SIMS) [e.g., 14]. Here we have taken extreme care to avoid any glue (epoxy or crystal bond) and water during sample preparation by polishing dry single mineral grains maintained in place using a gecko style sticky material. Minerals are then cleaned with acetone and isopropanol. The planned sequence of analysis is FTIR, electron microprobe, and SIMS on each grain. So far, the Hyperion microscope of a Bruker FTIR at NASA-JSC has been used to detect O-H bonds in the minerals. Transmission FTIR analyses are made in the mid-infrared region with a polarizer and with varying aperture sizes (with sides of 20 to 100 μm and shape adapted to minimize analyzing inclusions and cracks). Water abundances can be calculated using the Beer-Lambert law with the absorbance area beneath the O-H bands and the measured sample thickness. Mineral specific absorption coefficients [15,16] are applied to polarized transmission spectra to calculate water contents. Given that infrared measurements in three mutually perpendicular orientations of an anisotropic mineral relative to the polarizer are necessary for quantification [17], water contents presented here are minimum values because analysis could be done in only two perpendicular orientations in each mineral grain.

Results:

The nakhlites analyzed so far are characterized by small amounts of water in their pyroxene (Figure 1): ≥ 9 ppm H_2O in Northwest Africa (NWA) 998, ≥ 0-4 ppm H_2O in Miller Range (MIL) 03346 and ≥ 1-19 ppm H_2O in NWA 6148. No water was detected in any nakhlite olivine. Pyroxene from Larkman Nunatak (LAR) 06319 has 0-24 ppm wt H_2O but olivine has no detectable water. No water was detected in Allan Hills (ALH) 84001 orthopyroxenes but 22 to 84 ppm H_2O is present in its maskelynite. Water contents are also variable within a single grain and between several grains from the same meteorite.

Discussion:

Our lack of water detection in Martian olivines is in contrast to olivine from enriched olivine shergottite Tissint for which 50-370 ppm wt H_2O are reported [14]. These water contents are high even when compared to most terrestrial olivines (mostly < 50 ppm H_2O; [12]). Moreover, hundreds of ppm wt H_2O have been reported in pyroxenes from epoxied thin sections of olivine-phyric shergottite Yamato 980459 (Y98), and nakhlites Nakhla and Lafayette [18], i.e., at least ten times more than we have measured in our meteorites.

The low water content we measured in Martian meteorite pyroxene is in contrast to that of typical terrestrial pyroxenes which rarely contain less then 25 ppm wt H_2O [e.g., [12,19-22]. The lack of correlation between water contents and major elements and the heterogeneity of water contents within and between pyroxene

grains is generally attributed to H loss by degassing. This could explain the low water contents of the Martian pyroxenes and the lack of water in the Martian olivines. Degassing is also evidenced in the apatites from MIL 03346 and NWA 5790 (paired with NWA 6148) [7]. For strongly shocked ALH 84001, H loss at impact may have played a role. Alternatively, the Martian mantle from which these Martian magmas originated from is drier than that of Earth. This latter explanation is consistent with the low water content in one melt inclusion from Y98 that has a Martian mantle H isotopic signature [23] and with apatite analysis in shergottites with no evidence of crustal contamination [9]. These studies suggest that the Martian mantle has a lower water content (< 73 ppm wt H_2O) than the terrestrial upper mantle (~200 ppm wt H_2O). We plan on expanding our dataset of H contents and isotopes, major and trace element concentrations to decipher the origin of the low water contents measured in Martian nominally anhydrous minerals.

References:

[1] Malin & Edgett (2000) *Science*, 288, 2330-2335.
[2] Smith (2002) *JGR*, 107, 25-21-25-19.
[3] Villanueva *et al.* (2015) *Science*, 348, 218-221.
[4] Mustard *et al.* (2008) *Nature*, 454, 305-309.
[5] Ehlmann *et al.* (2011) *Nature*, 479, 53-60.
[6] Greenwood *et al.* (2008) *GRL*, 35, L05203.
[7] McCubbin *et al.* (2013) *MAPS*, 48, 819-853.
[8] McCubbin *et al.* (2014) *AM*, 99, 1347-1354.
[9] McCubbin *et al.* (2016) *MAPS*, 51, 2036-2060.
[10] Boyce *et al.* (2014) *Science*, 344, 400-402.
[11] Bell (1992) *Nature*, 357, 646-647.
[12] Peslier (2010) *JVGR*, 197, 239-258.
[13] Boctor *et al.* (2003) *GCA*, 67, 3971-3989.
[14] Mane *et al.* (2016) *MAPS*, 51, 2073-2091.
[15] Bell *et al.* (1995) *AM*, 80, 465-474.
[16] Mosenfelder *et al.* (2015) *AM*, 100, 1209-1221.
[17] Libowitzky & Rossman (1996) *PCM*, 23, 319-327.
[18] Tucker *et al.* (2014) *LPSC*.
[19] Xia *et al.* (2013) *EPSL*, 361, 85-97.
[20] Mosenfelder & Rossman (2013) *AM*, 98, 1042-1054.
[21] Mosenfelder & Rossman (2013) *AM*, 98, 1042-1054.
[22] Liu *et al.* (2015) *JP*, 56, 681-702.
[23] Usui *et al.* (2012) *EPSL*, 357-358, 119-129.

Figure 1: Examples of FTIR spectra of Martian minerals in the O-H region and normalized to 1-cm thickness. The two spectra shown for each mineral correspond to two analyses performed at the same location in the mineral grain but with the IR polarizer oriented in two perpendicular directions. The fact that the O-H bands only show for one direction of the polarizer in the pyroxene (px) demonstrate that this water is H in the px lattice (as opposed to water in a fluid or glass inclusion for example).